Visible light photocatalytic reduction of Cr(VI) on TiO$_2$ in situ modified with small molecular weight organic acids

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ABSTRACT

Visible light photoreduction of toxic Cr(VI) over TiO$_2$ was achieved through surface modification with small molecular weight organic acids (SOAs) as sacrificial organics. Because neat anatase TiO$_2$ is active only under UV light irradiation ($\lambda < 387$ nm), no photoreduction of Cr(VI) was observed in TiO$_2$ dispersions being irradiated with visible light ($\lambda > 420$ nm). However, when a small amount of colorless SOAs was added into the TiO$_2$ dispersion, a charge-transfer-complex (CTC) was formed between TiO$_2$ and SOA, which was sensitive to visible light irradiation and induced the photo-oxidation of SOA and photoreduction of Cr(VI). It was observed that about 95% of added Cr(VI) (0.2 mmol L^{-1}) was removed in the visible light-illuminated TiO$_2$ (1.0 g L^{-1}) dispersions at pH 3.0 within 2 h by adding 0.2 mmol L^{-1} tartaric acid as a SOA. The SOA-induced photoreduction of Cr(VI) proceeded via a CTC-mediated path, being governed by chemical structures of sacrificial SOAs. A higher energy of the highest occupied molecular orbital or lower ionization potential of SOAs is favorable to electron transfer within TiO$_2$-SOA complex, thereby accelerating the photoreduction of Cr(VI). The Cr(VI) removal was further enhanced by increasing SOA concentration and/or decreasing solution pH.

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1. Introduction

Chromium (VI) is a common toxic pollutant in wastewaters originating from various industrial processes such as electroplating, pigment production, and leather tanning. Because of carcinogenesis, mutagenesis and high mobility of Cr(VI), its concentration in drinking water has been regulated legislatively to be less than 0.05 mg L^{-1} in many countries such as Germany, Sweden Argentine, and China [1]. Therefore, the elimination of Cr(VI) is of great importance in the view of environmental security. Recently, increasing attention has been paid to the TiO$_2$ heterogeneous photocatalytic reduction process [2–6], in which Cr(VI) is reduced to less harmful and immobile Cr(III), followed by the combination with other effective separation method to yield a practical technology for removing toxic metals from wastewaters.

When the TiO$_2$ suspension was irradiated with the UV light ($\lambda < 387$ nm), the photo-induced electrons are responsible for the photocatalytic reduction of Cr(VI). The UV photocatalytic reduction of Cr(VI) to Cr(III) generally proceeds very slowly, because the accompanyi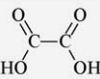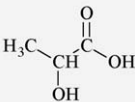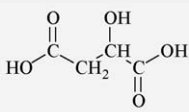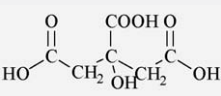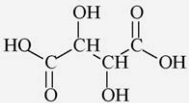ng oxidation of water to oxygen is a kinetically slow process [1]. It has been reported that the addition of organic donors accelerates significantly the UV photocatalytic reduction of Cr(VI), due to the enhanced charge separation of photo-induced hole/electron pairs by the simultaneous reduction/oxidation reactions [2–5]. We have found that the photocatalytic reduction of Cr(VI) under UV irradiation was dependent on both of specific surface area and crystalline structure of TiO$_2$ in the absence of any organic compounds, but was dominated by the specific surface area of TiO$_2$ in the presence of organic compounds [7]. Because UV radiation takes up only less than 5% of solar energy, another effort has been devoted to improve the intrinsic efficiency of TiO$_2$ for Cr(VI) reduction under visible light irradiation. One of the most promising methods is the surface modification of TiO$_2$, especially, through an in situ method by direct adding appropriate compounds into TiO$_2$ dispersion during the photoreaction. Kyung et al. found that the visible light photoreduction of Cr(VI) over TiO$_2$ was accelerated by adding dyes via a dye-sensitization process [8]. A similar sensitization approach was also successfully applied to remove Cr(VI) in a visible light-illuminated aqueous solution of polyoxometalate [9]. Cho reported a surfactant-TiO$_2$ photochemical system, where TiO$_2$ exhibited a visible light activity for the Cr(VI) reduction in the presence of nonionic surfactant having polyoxyethylene groups (Brij) [10]. Recently, we investigated the structure–reactivity correlation in the visible light photodegradation of colorless aromatic pollutants over neat

Table 1
Comparisons between E_{HOMO} and AIP of SOAs, and photo-conversion of Cr(VI) within 5 h and dark adsorption of Cr(VI) on TiO_2 surface in the absence and presence of 0.1 mmol L^{-1} SOA at pH 3.0.

Properties of SOAs				Photo-conversion of Cr(VI) (%)	Dark adsorption of Cr(VI) (mg g^{-1})
Name	Structure	E_{HOMO} (a.u.)	AIP (a.u.)		
Blank		–	–	0.00	3.48
Oxalic acid		−0.2520	0.3710	0.00	1.56
Formic acid		−0.2562	0.4082	9.26	2.70
Lactic acid		−0.2409	0.3425	54.2	3.80
Malic acid		−0.2458	0.3369	76.8	3.08
Citric acid		−0.2441	0.3318	88.1	1.32
Tartaric acid		−0.2368	0.3247	92.1	2.60

TiO_2 via a charge-transfer-complex (CTC)-mediated pathway [11]. It is worth noting that the addition of Cr(VI) or H_2O_2 enhanced the degradation and mineralization of the tested aromatic pollutants, because the added Cr(VI) or H_2O_2 functioned as appropriate electron scavenger, markedly depressed the backward recombination of photo-injected electrons and the organic radicals on the surface of TiO_2 [11]. Accompanying the oxidation of the colorless aromatic organics, Cr(VI) was photo-catalytically reduced. Thus, we can anticipate that such a CTC-process can be applied to remove toxic Cr(VI) over neat TiO_2 under visible light. Due to the toxicity and possible incomplete mineralization of the dyes or colorless aromatic compounds, there is a risk of secondary contamination in the treatment of Cr(VI). Thus, it is necessary to find better sacrificial organic agents. Similar CTC-mediated pathway has been observed in visible light-induced TiO_2 photocatalysis of chlorophenols, phenolic compounds and fluoroquinolone antibacterial agents [11–15]. It is interesting that the above-mentioned colorless aromatic substrates share a similarity in containing phenolic and/or carboxylic acid moieties, which are beneficial to the complex formation by hydroxyl and/or carboxyl groups. For this reason, some small molecular weight organic acids (SOAs) containing these functional groups should merit special attention. Particularly, the dicarboxylic acids and α-hydroxyl carboxylic acids such as oxalic and lactic acid may strongly bind on TiO_2 surface via ester linkages or in a bidentate chelate fashion [16]. Moreover, it is known that these SOAs are nontoxic and ready for full mineralization, and it is expected that as green sacrificial agents these SOAs may induce visible light photocatalytic reduction of Cr(VI) over neat TiO_2. Therefore, the goals of the present work are to investigate the visible light photocatalytic reduction of Cr(VI) in the presence of different SOAs and to understand the related reaction mechanism.

2. Experiments

2.1. Materials

Pure anatase TiO_2 powders (average size 15 nm, BET area, 180.9 m^2 g^{-1}; Zhoushan Nano Company, China) were used as the photocatalyst, because this catalyst has larger specific surface area and better photocatalytic activity than Degussa P25 in the simultaneous photocatalytic treatment of Cr(VI) and organic pollutants under either UV or visible light irradiation as reported previously [7,11]. Some SOAs including formic acid, oxalic acid, lactic acid, malic acid, citric acid and tartaric acid (TA) were used as sacrificial organics and their structural formulae were shown in Table 1. All the chemical reagents were of analytical reagent grade and used as received. Distilled water was used throughout the experiment. Solution pH was adjusted with H_2SO_4 and NaOH solutions (1.0 mol L^{-1}).

2.2. Photo-reactor and light source

A 500-W halogen lamp as the source of visible light was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp. An edge filter with the cut-on wavelength of 460 nm at 50% of peak transmission was placed outside the Pyrex jacket to completely remove any radiation below 420 nm. By using a Digital Lux Meter (ST-80C, Beijing Normal University photoelectric instrument Co. Ltd), the

intensity of light in the photo-reactor was measured to be ca. 3.0×10^4 lx.

2.3. Procedures and analysis

For typical photocatalytic runs, TiO$_2$ (0.05 g) was suspended into 50 mL aqueous solution of Cr$_2$O$_7^{2-}$ (0.1 mmol L^{-1}) with or without the addition of SOAs. Prior to the irradiation, the suspension was first sonicated for 60 s, and then magnetically stirred in the dark for ca. 15 min to ensure the establishment of adsorption–desorption equilibrium of the concerned compounds on TiO$_2$ surface. The concentration of Cr(VI) after equilibration was measured and taken as the initial concentration (c_0), to discount the adsorption in the dark. The reaction mixture was maintained in suspension by using a magnetic stirrer before and during the irradiation.

At appropriate time intervals, 2 mL aliquots were sampled, immediately centrifuged at 14,000 rpm for 15 min, and then filtered through a 0.22-μm pore size filter to remove the TiO$_2$ particles. The filtrates were collected and analyzed. The concentration of Cr(VI) was determined by using the diphenyl carbazide colorimetric method at 540 nm (GB 7466-87, Standards of China) on a Cary 50 UV–vis spectrophotometer (Varian). Triplicate runs were carried out for each test, and the relative standard deviation was generally less than 5%.

The interaction between SOAs and TiO$_2$ surface was examined by UV–vis diffuse reflectance spectroscopy (DRS). TiO$_2$ suspensions (2.0 g L^{-1}) were prepared at pH 3.0 with the addition of 0.2 mmol L^{-1} SOA and/or 0.2 mmol L^{-1} Cr(VI) and set for overnight in the dark. After the solids were collected by vacuum-filtration with a filter (0.22 μm) and dried in dark at room temperature, their DRS spectra were measured on a UV-2550 spectrometer (Shimadzu) equipped with an integrating sphere attachment, using BaSO$_4$ as background.

2.4. Computational methods

The energies of the highest occupied molecular orbital (E_{HOMO}) and adiabatic ionization potential (AIP) of tested organic acid were calculated by using the Amsterdam Density Functional (ADF) program package ADF2007.01 [17]. The Slater-type orbitals (STOs) basis set employed is the standard ADF-TZP, which is triple-ζ for valence orbitals plus one polarization function. The exchange-correlation potential is based on the Vosko–Wilk–Nusair (VWN) [18] local density functional plus the PW91 [19] generalized gradient approximations (GGA).

3. Results and discussion

3.1. Promoted visible light photocatalytic reduction of Cr(VI) by adding tartaric acid

Fig. 1 illustrates the dark adsorption of Cr(VI) and the photocatalytic conversion of Cr(VI) removal over TiO$_2$ in the absence and presence of 0.1 mmol L^{-1} TA. It is easily seen from Fig. 1a that Cr(VI) is able to be adsorbed on the surface of TiO$_2$ and the adsorption/desorption equilibrium is achieved rapidly (within less than 10 min) under the tested conditions, being attributed to the strong electrostatic attraction between the anionic chromate species (HCrO$_4^-$ and/or Cr$_2$O$_7^{2-}$) and the positively charged surface of TiO$_2$ at pH 3.0 [20]. At the equilibrium state, about 35% of 0.2 mmol L^{-1} Cr(VI) is adsorbed on TiO$_2$. Because the competitive adsorption of TA may weaken the electrostatic attraction between anionic chromate species and the positively charged TiO$_2$ surface, the addition of TA decreases slightly the adsorption amount of Cr(VI).
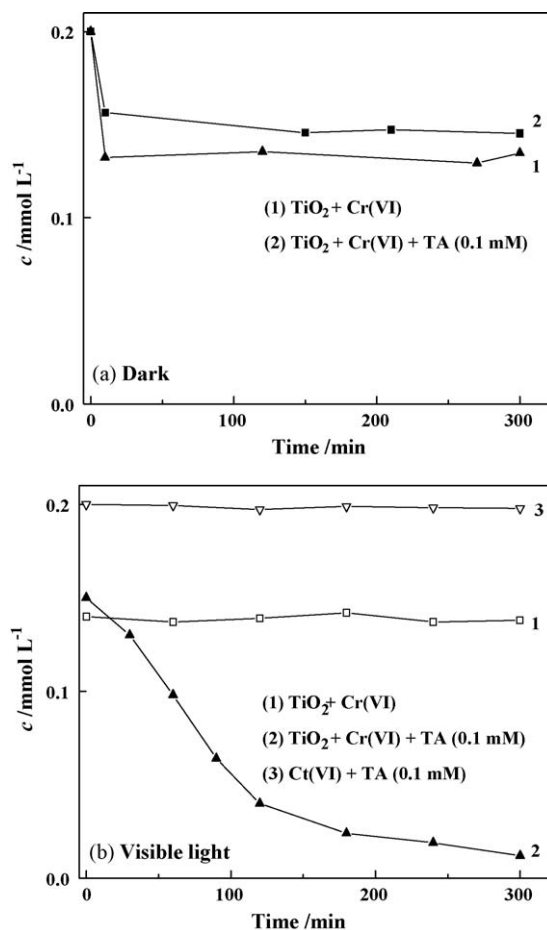

Fig. 1. (a) The adsorption of Cr(VI) in the dark and (b) the visible light photoreduction of Cr(VI) over TiO$_2$ (1.0 g L^{-1}) in the absence (1) and presence (2) of 0.1 mmol L^{-1} TA at pH 3.0. As a control, curve 3 in (b) represents the Cr(VI) decay in TiO$_2$-free TA-containing solution under visible light irradiation.

In consideration of the fast adsorption/desorption equilibrium, the photocatalytic reduction of Cr(VI) over TiO$_2$ was investigated after a pre-setting of 15 min for achieving the adsorption–desorption equilibrium and the possible decrease in Cr(VI) in the solution due to the adsorption was discounted in the calculated removal of Cr(VI) by the photocatalytic process. As shown in Fig. 1b, more than 90% of the added 0.2 mmol L^{-1} Cr(VI) is converted within 5 h of visible light illumination in the simultaneous presence of 1.0 g L^{-1} TiO$_2$ and 0.1 mmol L^{-1} TA (curve 2 in Fig. 1b). Although Tzou et al. previously found that 0.2 mmol L^{-1} citric acid or oxalic acid could slowly reduce the micromolar levels of Cr(VI) (40 μmol L^{-1}) within 120 h at pH 2.5 under fluorescent light [21], our present work showed that the photoreduction of Cr(VI) (0.2 mmol L^{-1}) under visible light irradiation was negligible in the presence of either TA (0.1 mmol L^{-1}) alone or only TiO$_2$ photocatalyst (1.0 g L^{-1}) within 5 h (curves 1 and 3 in Fig. 1b). Thus, the significant removal of Cr(VI) in the system of TiO$_2$-TA-Cr(VI) under visible light irradiation demonstrates that the addition of TA triggers the visible light photocatalytic reduction of Cr(VI) over neat TiO$_2$. Similar phenomena were observed when other SOAs such as formic, lactic, malic and citric acid were added into the Cr(VI)-containing TiO$_2$ dispersions under visible light illumination conditions (see Section 3.2). This demonstrates that these SOAs indeed participate in the visible light photocatalytic reduction of Cr(VI) over TiO$_2$. Because neither neat TiO$_2$ nor the tested SOAs have absorptions in the visible light region, the visible light photoreduction of Cr(VI) in the presence of SOAs may be
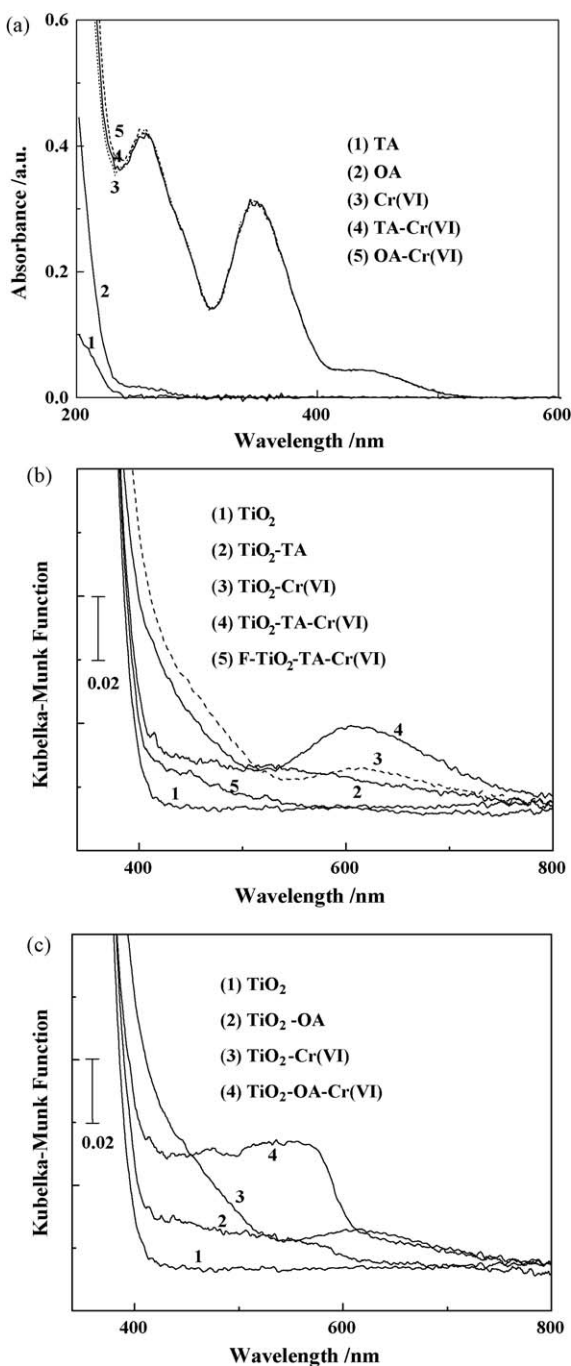
Fig. 2. UV–vis absorption (a) and DRS (b, c) spectra of the single, binary and ternary systems composed of SOA, Cr(VI) and TiO_2. Curve 5 in (b) shows the DRS spectrum of TiO_2-TA-Cr(VI) in the presence of 10.0 mmol L^{-1} NaF. OA in the figure represents oxalic acid.

attributed to a charge-transfer-complex (CTC)-mediated photo-catalytic process. This is similar to the previously reported observations, where colorless aniline, phenolic or fluoroquinolone compounds adsorb on TiO_2 surface to form the charge transfer complex, which can be photo-excited upon absorption of visible light to initiate a direct electron transfer from the surface-complexed organics to the TiO_2 conduction band (CB), resulting in the photocatalytic degradation of compounds over neat TiO_2 under visible light irradiation ($\lambda > 420$ nm) [11–15].

The possible CTC-mediated photocatalytic mechanism requires a fairly strong interaction between TiO_2 and SOAs. Therefore, the UV–vis diffuse reflectance spectra (DRS spectra) were recorded to

investigate the electronic interaction between TiO_2 and SOAs in the absence and presence of Cr(VI). As shown in Fig. 2, neither the tested SOAs nor TiO_2 can absorb visible light (curves 1 and 2 in Fig. 2a, and curve 1 in Fig. 2b), and the UV–vis absorption spectrum of Cr(VI) shows one weak visible absorption band near 420 nm and two strong characteristic UV absorption bands (curve 3 in Fig. 2a). Accordingly, the adsorbed Cr(VI) increases significantly the absorption of TiO_2 at $\lambda > 400$ nm, mainly due to the absorption of Cr(VI) itself (curve 3 in Fig. 2b and c) [22]. However, no Cr(VI) photoreduction is observed in TiO_2 suspensions without SOAs after an irradiation of 5 h (curve 1 in Fig. 1b), because the adsorbed Cr(VI) cannot cause the inherent TiO_2 to be photo-excited by visible light and consequently no photo-induced electron are produced in TiO_2 CB for the Cr(VI) reduction. On the other hand, once the SOA molecules are adsorbed on TiO_2 surface, the DRS spectrum of TiO_2 is red shifted into the visible light region (curve 2 in Fig. 2b and c), implying a surface complex is formed on the surface of SOA-adsorbed TiO_2 nanoparticles, which yields an absorption band near 450 nm, being assigned to the ligand-to-metal charge-transfer (LMCT) transition within the surface complexes [23]. Particularly, a stronger visible light absorption was observed in the TiO_2-SOA-Cr(VI) ternary system, being inconsistent with the sum total of that in TiO_2-SOA, TiO_2-Cr(VI) and SOA-Cr(VI) binary systems (curve 4 in Fig. 2b and c). It is also noted the absorption spectrum of the mixture of SOA and Cr(VI) (curves 4 and 5 in Fig. 2a) is proximately equal to the sum of their individual spectra, being indicative of no observable interaction between Cr(VI) and the tested SOAs. Together with no chemical interaction between Cr(VI) and TiO_2 (curve 3 in Fig. 2b and c), it is supposed that the visible light absorption of TiO_2-SOA-Cr(VI) is mainly attributed to the TiO_2-SOA complex and Cr(VI), and the co-existence of Cr(VI) significantly increases the absorption of the TiO_2-SOA complex in the visible light region.

When the TiO_2 suspension containing both SOA and Cr(VI) is exposed to visible light, the absorbed photons will initiate electron transfer from the HOMO of SOA to TiO_2 CB, resulting in the formation of radical anions ($RCOO^{\bullet-}$), which is similar to that in previously proposed CTC-mediated process [11–15]. And then, the electrons being transferred into TiO_2 CB either recombine with adsorbed organic radicals or are delivered to electron acceptors (dissolved O_2 or adsorbed Cr(VI)). Our previous study demonstrated that the presence of Cr(VI) could depress markedly the backward charge recombination [11]. Besides, we carried out the similar experiments by purging N_2 and found that the dissolved O_2 had a negligible effect on the photoreduction of Cr(VI). This is mainly due to the stronger electrostatic attraction between anionic chromate species ($HCrO_4^-$ and/or $Cr_2O_7^{2-}$) and the positively charged surface of TiO_2 at pH 3.0, together with its more positive redox potential ($E^\circ(Cr_2O_7^{2-}/Cr^{3+}) = 1.35$ V, $E^\circ(O_2/O_2^{\bullet-}) = -0.32$ V vs NHE), which increases the competing ability of the Cr(VI) reduction in comparison with dissolved O_2 for trapping electrons, and consequently enhances the charge separation. Moreover, the addition of a relatively small amount of TA (0.1 mmol L^{-1}) can reduce more than 90% of 0.2 mmol L^{-1} Cr(VI) to Cr(III) over TiO_2 within 5 h under visible light illumination (curve 2 in Fig. 1b), implying that one TA molecule can donor successively several electrons for the Cr(VI) photoreduction. It is known that the general organic radicals, especially $CO_2^{\bullet-}$ radicals, have more negative redox potentials ($E^\circ(CO_2^{\bullet-}/CO_2) = -1.90$ V, $E^\circ(R_1^{\bullet+/-}/R_2^{\bullet+/-}) < 1.0$ V) [11,24], which means that the intermediate organic radicals are thermodynamically capable of reducing Cr(VI), leading to the accompanying oxidation of organic radicals to smaller organic radicals and even their mineralization to CO_2 and H_2O. This proposal is further supported by the previous report that $CO_2^{\bullet-}$ radicals could directly reduce metal ions (i.e. Cd^{2+}, Zn^{2+}, Mn^{2+}) and methyl viologen [24,25], and our recent observation that the

addition of Cr(VI) accelerated greatly the mineralization of salicylic acid in the visible light-illuminated TiO₂ dispersions via the CTC-mediated pathway [11]. Thus, the CTC-mediated path between SOAs and TiO₂ may provide an alternative efficient approach to reduce Cr(VI) over neat TiO₂ under visible light irradiation.

3.2. Effect of chemical structure of small organic acids on visible light photoreduction of Cr(VI)

Fig. 3 compares the visible light photoreduction of Cr(VI) in TiO₂ suspensions containing 0.1 mmol L⁻¹ of various SOAs. In the control experiments, it was confirmed that all the tested SOAs could neither directly photoreduce Cr(VI) in visible light-illuminated solution without TiO₂ photocatalyst nor chemically reduce Cr(VI) by the SOA themselves in TiO₂ dispersions in dark, thus the disappearance of Cr(VI) in TiO₂-SOA-Cr(VI) system under visible light illumination should be attributed to the above-mentioned CTC-mediated photocatalytic process. From Fig. 3, it is easily seen that the rate of Cr(VI) reduction in the presence of SOAs has the order of oxalic acid < formic acid < lactic acid < malic acid < citric acid < TA. Of the tested SOAs, TA is the most efficient, but oxalic acid cannot induce observable photoreduction of Cr(VI) over TiO₂. This hints that the visible light photoreduction of Cr(VI) over TiO₂ is strongly dependent on the chemical structure of SOAs. It is similar to the previously reported phenomena that different photoreduction rates of Cr(VI) over TiO₂ were observed in the presence of different organic compounds under UV or fluorescent light illumination [7,26]. Upon exposure to the UV or fluorescent light illumination, the reduction rate of Cr(VI) over TiO₂ by photo-induced electrons is limited by the coupled photo-oxidation of the added sacrificial organics, which can either be attacked by photo-induced holes or be oxidized by generated •OH radicals. The organic compounds have different abilities of trapping holes and/or •OH, leading to the chemical structure dependence of the reduction rate of Cr(VI) under UV or fluorescent light. However, this proposal cannot rationally explain why the Cr(VI) photoreduction depends on the added organics under visible light illumination, because neither TiO₂ photocatalyst nor SOAs alone can photoreduce Cr(VI) under visible light illumination as observed in Fig. 1b. Thus, the photoreduction of Cr(VI) under visible light must be originated from the chemical interaction between SOAs and TiO₂, including the formation of surface complex, electron transfer and so on.

To clarify the influences of the chemical structures of the added SOAs on the visible light photoreduction of Cr(VI), we investigated the dark adsorption of Cr(VI) in the presence of different SOAs.
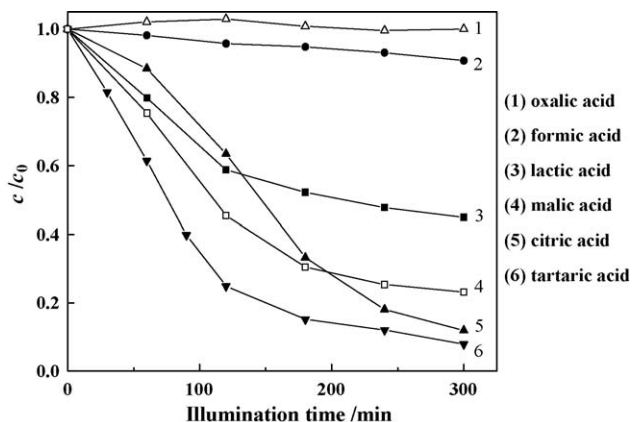

Fig. 3. Photocatalytic reduction of Cr(VI) over TiO₂ (1.0 g L⁻¹) under visible light illumination in the presence of different SOAs (0.1 mmol L⁻¹) at pH 3.0, curves 1–6 represent the addition of oxalic, formic, lactic, malic, citric, and tartaric acids, respectively.

Table 1 shows that most of the tested SOAs decrease the adsorption of Cr(VI) over TiO₂, because of the competitive adsorption of SOAs on the surface of TiO₂. It is also found the adsorbed amount of Cr(VI) on TiO₂ in the presence of different SOAs increases in the observed order: citric acid < oxalic acid < TA < formic acid < malic acid < lactic acid, being different from the change tendency for the rate of Cr(VI) reduction. This implies that the effects of added organic acid for the visible photocatalytic reduction of Cr(VI) is not governed by the Cr(VI) adsorption over TiO₂.

Since the visible light reduction of Cr(VI) was induced by a CTC-mediated path as discussed in Section 3.1, the formation of surface complexes plays a very important role in the visible light photoreduction of Cr(VI), which is influenced mainly by the chemical structure of SOAs. DRS analysis confirmed that there was a strong interaction between the organic compound and TiO₂ surface for all the tested SOAs. The absorption of TiO₂-SOAs in visible region is slightly increased in the order of formic acid, oxalic acid, malic acid < citric acid, lactic acid < TA, being well inconsistent with the changed tendency for the rate of Cr(VI) reduction. Moreover, although no reduction of Cr(VI) was observed in the system of TiO₂-oxalic acid (curve 1 in Fig. 3), the added oxalic acid can also form a visible light absorbing surface complex on the surface of TiO₂ in both the absence and presence of Cr(VI), as evidenced by the DRS spectrum in Fig. 2c. This may hint that not only the formation of surface complexes but also some other factors influence the Cr(VI) reduction. In a recent study, we reported that the formation of surface complexes was a primary requisite and the subsequent charge transfer within the surface complexes was also an essential process for the photodegradation of colorless aniline and phenolics over neat TiO₂ under visible light irradiation [11]. Thus, two important properties being associated with intramolecular electron transfer (i.e. E_{HOMO} and AIP of SOAs) are further studied to reveal the reason for the dependence of Cr(VI) reduction on the chemical structure of SOAs.

As shown in Table 1, the calculated E_{HOMO} is increased in the order of formic acid < oxalic acid < malic acid < citric acid < lactic acid < TA, and the calculated AIP is accordingly decreased in the order of TA < citric acid < malic acid < lactic acid < oxalic acid < formic acid. It is found from Fig. 4 that there are proximate linear correlations between the Cr(VI) conversion (η, %) and either E_{HOMO} or AIP of SOAs with the regression equations of $\eta = 1215.2 + 4723.5 E_{HOMO}$ ($R = 0.79$) and $\eta = 450.03 - 1125.1$ AIP ($R = 0.85$). This means that the Cr(VI) reduction via the CTC-mediated process is mainly affected by the E_{HOMO} and AIP of SOAs. This proposal is also supported by the previous report that the visible degradation rate of colorless aniline and phenolic pollutants over TiO₂ via a CTC-mediated pathway was linearly increased with the increase in the energy of HOMO or decreasing ionization potential of organics [11]. As the value of E_{HOMO} is increased, the energy gap between HOMO of SOAs and TiO₂ CB is enlarged, leading to enhancing the driving force of photo-induced electron transfer within TiO₂-SOA complexes. On the other hand, as the ionization potential is increased, it becomes more difficult to remove an outermost electron. Thus, a high E_{HOMO} or low AIP is beneficial to enhance the electron transfer, leading to accelerated rates of electron transfer into the TiO₂ CB, which then delivers the electron to Cr(VI), thereby resulting in the enhancement of Cr(VI) reduction.

3.3. Effects of reaction parameters on the visible light photoreduction of Cr(VI)

The visible light photoreduction of Cr(VI) is influenced by a series of reaction parameters, and here the effects of the SOAs concentration and solution pH were investigated as two of the most important reaction parameters. Since TA is the most efficient sacrificial agent for Cr(VI) reduction among the tested SOAs,
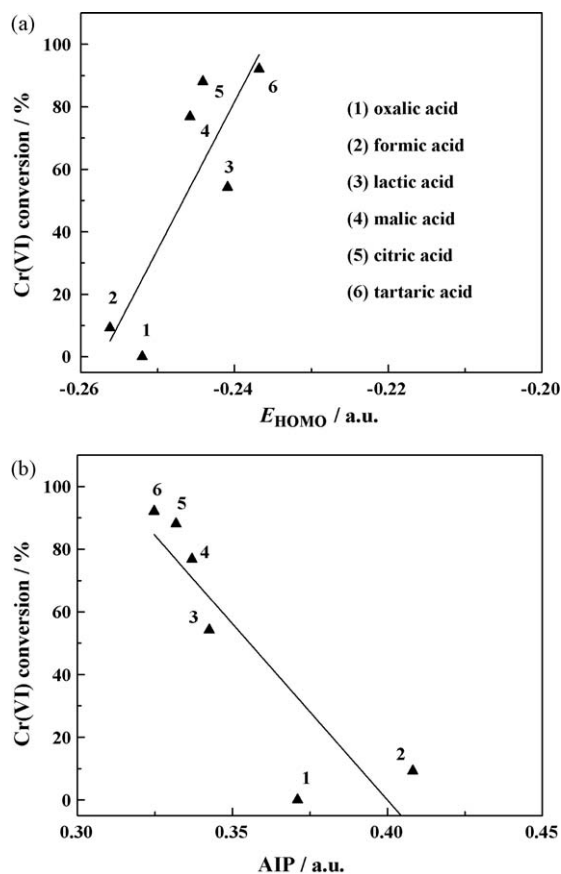
Fig. 4. Relationships between the Cr(VI) conversion and E_{HOMO} (a) or AIP (b) of the tested SOAs. Numbers 1–6 represent oxalic, formic, lactic, malic, citric, and tartaric acids, respectively. The Cr(VI) conversion was obtained in visible light-illuminated TiO$_2$ (1.0 g L^{-1}) dispersions containing 0.1 mmol L^{-1} SOAs within 5 h.
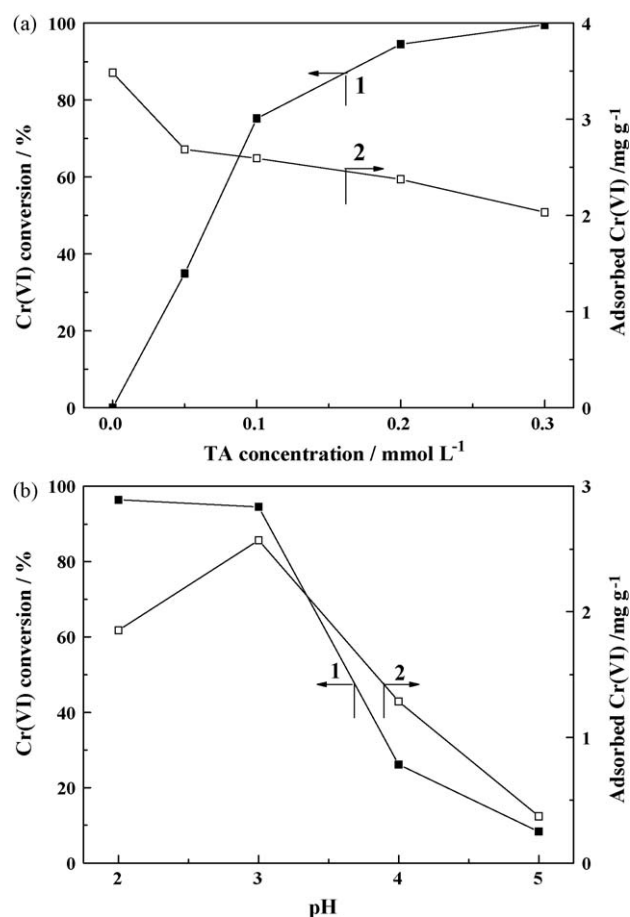

Fig. 5. Effects of (a) initial concentration of TA and (b) solution pH on (1) the visible photocatalytic reduction of Cr(VI) within 2 h and (2) the dark adsorption amount of Cr(VI) over TiO$_2$ (1.0 g L^{-1}). Solution pH in (a) is fixed at 3.0 and the addition of TA is 0.2 mmol L^{-1} in (b).

further experiments were performed using TA as the organic additive. Before such tests, it was first confirmed in control experiments that no visible light-induced photoreduction of Cr(VI) was observed in the presence of TA alone within 5 h at all the concerned solution pH values and TA concentrations, where the lowest tested solution pH was pH 1.0 and the highest concentration of TA was 1.0 mmol L^{-1}.

Fig. 5a illustrates the photocatalytic reduction of Cr(VI) over TiO$_2$ with various initial concentrations ($c_{0,TA}$) of TA. As $c_{0,TA}$ is increased from 0 to 0.3 mmol L^{-1}, the Cr(VI) conversion within 2 h is significantly increased from 0% to 99.5%, whereas the adsorption of Cr(VI) on the surface of TiO$_2$ is decreased from 3.48 to 2.03 mg g^{-1}. The competitive adsorption of TA on the TiO$_2$ surface is unfavorable to the adsorption of Cr(VI), but the adsorption of Cr(VI) in the presence of TA is strong enough to support a fast photoreduction of Cr(VI). This hints that the adsorption of TA is more important than the adsorption of Cr(VI) to the visible light photoreduction of Cr(VI). The photoreduction of Cr(VI) is accelerated with the increased addition of TA in the tested range of TA concentrations.

The effect of pH on the TiO$_2$-photocatalytic reduction of Cr(VI) in the presence of 0.2 mmol L^{-1} TA was examined under visible light irradiation. It is easily seen from Fig. 5b that as solution pH value is decreased from 5 to 2, the Cr(VI) reduction rate is significantly enhanced and then approaches an almost constant value at pH ≤3. A similar phenomenon was observed in our previous report that the photodegradation rate of colorless salicylic acid over TiO$_2$ via a CTC-mediated path had a maximum value at pH 3.0 [11]. The pH effect on the Cr(VI) conversion is

mainly ascribed to the following three reasons. Firstly, the adsorption of organic acid is a typical chemisorption of complexing anion and it is favorable to the formation of surface complex at the first pK_a of organic acid [23], namely around pH 3.0 for TA. Thus, the Cr(VI) photoreduction increases with decreasing pH and levels off in the range of pH 2.0–3.0. Secondly, solution pH influences the Cr(VI) adsorption. At pH <2, the neutral chromic acid molecule (H$_2$Cr$_2$O$_4$) is the dominant species of Cr(VI), whereas Cr(VI) exists as negatively charged HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ ions at pH >2 [20,27]. On the other hand, since the zero charge point for TiO$_2$ is ca. pH 6.0–6.4, the TiO$_2$ surface carries more positive charges as pH is decreased from 5.0 to 2.0, which greatly enhanced the electrostatic interaction between TiO$_2$ and anionic Cr(VI), leading to enhance the Cr(VI) adsorption. It is also noted that the neutral H$_2$CrO$_4$ species exhibit a lower affinity for the positively charged TiO$_2$ surface in comparison with the negatively charged Cr(VI) species [20,27]. Accordingly, the amount of adsorbed Cr(VI) on the TiO$_2$ surface is decreased to 0.37 mg g^{-1} at pH 5.0, only being 14.4% of the maximum value (2.57 mg g^{-1}) at pH 3.0 (curve 2 in Fig. 5b). Thus, increasing pH would decrease the photocatalytic reduction of Cr(VI). Thirdly, solution pH affects the thermodynamic driving force for the photoreduction of Cr(VI), which is related with the potential difference between the Cr(VI)/Cr(III) redox couple and electron donors including TiO$_2$ CB or organic radicals. For example, as solution pH is increased from 0 to 7, the value of $E°(Cr^{6+}/Cr^{3+})$ is decreased from 1.35 to 0.38 V with a pH dependence of −0.138 V/ pH unit at 25 °C, whereas the energy level of TiO$_2$ CB varies from −0.23 to −0.64 V with a pH dependence of −0.059 V/pH unit at
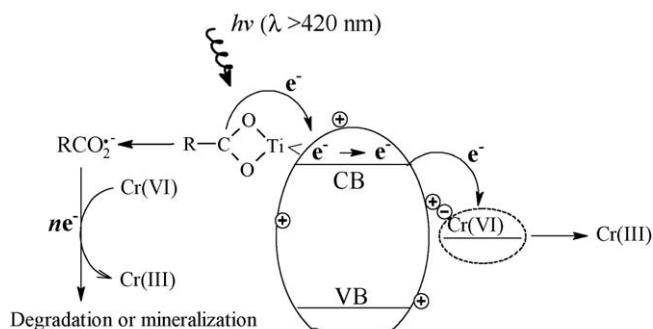
Scheme 1. SOA-induced photocatalytic reduction of Cr(VI) over neat TiO$_2$ under visible light irradiation via a charge-transfer-complex mediated pathway.

25 °C [4,27]. Thus, decrease in pH will increase the potential difference from 1.02 V at pH 7 to 1.58 at pH 0, being consequently beneficial to enhance the electron transfer power and accelerate the photocatalytic reduction of Cr(VI).

3.4. Reaction mechanism

The above discussion demonstrates that the visible light photocatalytic reduction of Cr(VI) in TiO$_2$ dispersion is able to be promoted with a CTC-mediated pathway by in situ adding some SOAs. As depicted in Scheme 1, the added SOA interacts with TiO$_2$ to form a surface complex TiO$_2$-SOA, which shows visible light absorption as evidenced by DRS analysis in Fig. 2. The visible light irradiation induces the intramolecular electron transfer from SOA moiety to TiO$_2$ CB, leading to the formation of organic radicals. Since the Cr(VI)/Cr(III) redox couple has a more positive reduction potential with respect to TiO$_2$ CB edge or RCOO$^{\bullet-}$ radicals [4,11], the injected electrons in TiO$_2$ CB are then delivered to the adsorbed Cr(VI), and the organic radicals can also react with Cr(VI), resulting in the photoreduction of Cr(VI) to Cr(III). Obviously, the formation of the TiO$_2$-SOA complex is of primary importance for the visible light activation, which is further supported by the inhibiting effect of NaF on Cr(VI) reduction. It is known that NaF favors the formation of a complex with TiO$_2$ by replacing surface hydroxyl groups [28,29]. Thus the formation of TiO$_2$-SOA complex is significantly prohibited on the fluorinated-TiO$_2$ surface (curve 5 of Fig. 2b). Accordingly, when NaF is present in the TiO$_2$-TA-Cr(VI)

Fig. 6. Effect of NaF on the photocatalytic reduction of Cr(VI) over TiO$_2$ (1.0 g L^{-1}) in the presence of TA (0.2 mmol L^{-1}) at pH 3.0 under visible light irradiation. (1) Blank, (2) 1.0 mmol L^{-1} NaF, (3) 10.0 mmol L^{-1} NaF.

system, the visible light photoreduction of Cr(VI) is dramatically depressed, and hence less than 10% of the added Cr(VI) was photoreduced within 5 h in the presence of 10.0 mmol L^{-1} NaF (curve 3 in Fig. 6). Moreover, another essential requisite for the Cr(VI) photoreduction is the efficiency of intramolecular electron transfer within TiO$_2$-SOA complexes, and intermolecular electron transfer between TiO$_2$ CB or organic radicals and Cr(VI). The former is mainly affected by the chemical structure of organic molecules as discussed in Section 3.2. The appropriate SOAs should possess a higher E_{HOMO} or lower AIP, which is favorable to electron transfer. The latter is mainly dependent on the Cr(VI) adsorption and the potential difference between electron donors (i.e. TiO$_2$ CB or organic radicals) and $E°(Cr^{6+}/Cr^{3+})$. Decreasing pH not only favors the Cr(VI) adsorption on TiO$_2$ but also increases the potential difference, thereby having a beneficial effect on the Cr(VI) photoreduction.

4. Conclusions

The photocatalytic reduction based on TiO$_2$ nanoparticles is a promising technique for the removal of toxic Cr(VI). As an extension to the catalytic process of TiO$_2$ under UV light, the present work investigated the photoreduction of Cr(VI) over neat TiO$_2$ under visible light irradiation. It was observed that the addition of appropriate SOAs such as tartaric, citric and lactic acids triggered the photoreduction of Cr(VI) over neat TiO$_2$, and the added Cr(VI) (0.2 mmol L^{-1}) could be almost completely removed within 2 h over TiO$_2$ (1.0 g L^{-1}) in the co-existence of 0.2 mmol L^{-1} TA at pH 3.0. The photocatalytic reduction of Cr(VI) was demonstrated to proceed a CTC-mediated path, in which the photo-generated electrons were transferred from SOAs to TiO$_2$ CB, and then delivered to the adsorbed Cr(VI) on TiO$_2$ surface, resulting in the reduction of Cr(VI) and the formation of organic radicals. Meanwhile, the generated organic radicals having highly reducing ability can make a contribution to the Cr(VI) photoreduction, leading to the oxidation of SOAs until their mineralization to CO$_2$ and H$_2$O. The chemical structure of SOAs, solution pH, and initial concentration of SOAs had strong influences on the Cr(VI) photoreduction. Either a higher energy of E_{HOMO} or low AIP favored the intramolecular charge transfer within surface complexes formed between SOAs and TiO$_2$, and consequently enhanced the photoreduction of Cr(VI). Because of the nontoxicity of SOAs and operation simplicity, the system of TiO$_2$-SOAs may provide an alternative way for the efficient removal of Cr(VI) under visible light irradiation.

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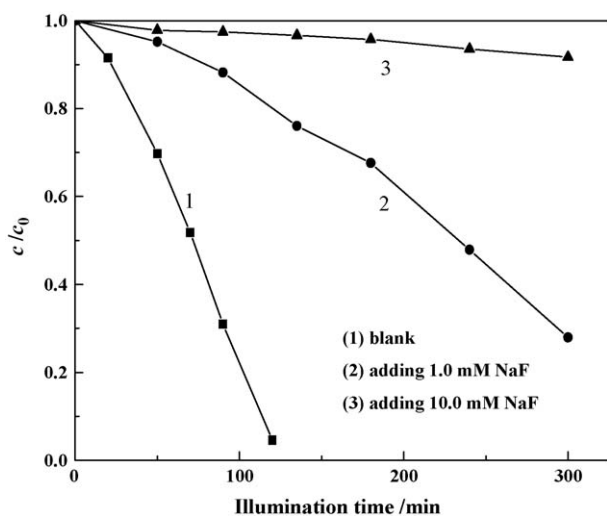[8] H. Kyung, J. Lee, W. Choi, Environ. Sci. Technol. 39 (2005) 2376.

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